Supplementary Information

Organic-Inorganic Hybrid Polyhedra That Can Serve as Supermolecular Building Blocks

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Materials and methods

All reagents were purchased in high purity grade from Fisher Scientific and used without further purification. Solvents were purified according to standard methods and stored in the presence of molecular sieves. Thermogravimetric analysis (TGA) was performed under nitrogen on a TA Instrument TGA 2950 Hi-Res. X-ray powder diffraction (XPD) data were recorded on a Bruker D8 Advance X-ray diffractometer at 20 kV, 5 mA for Cu_{kR} (λ = 1.5418 Å). The simulated XPD patterns were produced by using Mercury software. Gas adsorption was measured on the Micromeritics ASAP 2020 Surface Area and Porosity Analyzer**.** Mass spectrometry was collected on Bruker Daltronics Autoflex MALDI-TOF and Agilent 6540 Liquid Chromatography/Quadrupole Time-of-Flight Mass Spectrometer.

Synthetic procedures

Hyball-3: Reaction of H_3BTC (0.05 mmol) with VCl_3 (0.05 mmol) in 1.5 mL N,N-dimethylacetamide (DMA) and 0.5 mL H_2O at 105°C for 2 days affords dark green rhombic crystals of **Hyball-3** (washed with MeOH) with a yield of ~93% based on VCl_3.
Hyball-4: Reaction of H_3BTC (0.05 mmol) with VCl_3 (0.05 mmol) in 1.5 mL N,N-dibutylformamide (DBF) and 0.5 mL H_2O 105°C for 5 days affords dark green rhombic crystals of **Hyball-4** (washed with MeOH) with a yield of ~35% based on VCl_3.
Hyball-5: Reaction of H_3BTC (0.05 mmol) with VCl_3 (0.25 mmol) in 1.5 mL N,N-dimethylacetamide (DMA) and 0.5 mL H_2O affords dark green rhombic crystals of **Hyball-5** (washed with MeOH) with a yield of ~22% based on VCl_3.
Hyball-3′: Crystals of **Hyball-3** were exposed to atmosphere for 2 weeks, **Hyball-3'** was harvested.
Hyball-3-Ba: 10.0 mg **Hyball-3** was dissolved into 5.0 mL DMA and 1.0 mL H_2O by sonication and heating. $BaCl_2$ of 40.0 mg was dissolved into 5.0 mL MeOH. This $BaCl_2$ solution was layered on the **Hyball-3** solution. After 2 weeks, hexagonal green crystals were harvested and washed with MeOH (yield of ~20% based on **Hyball-3**).

Crystallography details

Hyball-3 was collected at the Advanced Photon Source on beamline 15ID-C of ChemMatCARS Sector 15 (λ = 0.40663 Å, T = 100(2) K). **Hyball-3′**, **-4** and **-5** were performed on an Oxford Supernova diffractometer at 293(2) K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using the ω-scan technique.. **Hyball-3-Ba** was collected with a Bruker-AXS SMART-APEXII CCD diffractometer (CuKα, λ = 1.54178 Å). Data integration and reduction were performed by using Saint Program. Scaling and absorption correction were performed by a multi-scan method implemented in SADABS. The structures were solved with SHELXS-97 (direct methods) and refined with SHELXL-97 (full-matrix least-squares on F^2) contained in the WinGX v1.70.01 program packages. Site occupancy of V sites in **Hyball-5** was determined through free refinement. Disordered molecules in the cavities of **Hyball-3**, **-4**, **-5** and **-3-Ba** were modeled as water molecules to improve the agreement indices. The contribution of disordered solvent molecules in **Hyball-3′** was treated as diffuse using the Squeeze procedure

implemented in Platon. (A. L. Spek, *J. Appl. Crystallogr.* 2003, **36**, 7; (b) P. Vander Sluis, A. L. Spek. *Acta Cryst.* 1990. **A46**, 194.) CCDC reference numbers 965262 to 965266 for complexes **Hyball-3**, **3′**, **-3-Ba**, **-5** and **-4**.

Gas Adsorption Experiments.

Low pressure gas adsorption isotherms of Hyballs were collected using the surface area analyzer ASAP 2020. Before the measurements, the freshly prepared sample was exchanged with methanol for 3 days. The sample was dried on the Schlenk line for overnight at room temperature and then degased by using the "outgas" functional of ASAP 2020 for 10 hours at 60 ^{o}C. N_2 sorption isotherms were measured at 77 K using a liquid N_2 bath. CO_2 sorption isotherms were collected at 195K by using acetone-dry ice bath. CO_2 and CH_4 sorption isotherms were measured at 298 and 273 K using water bath.

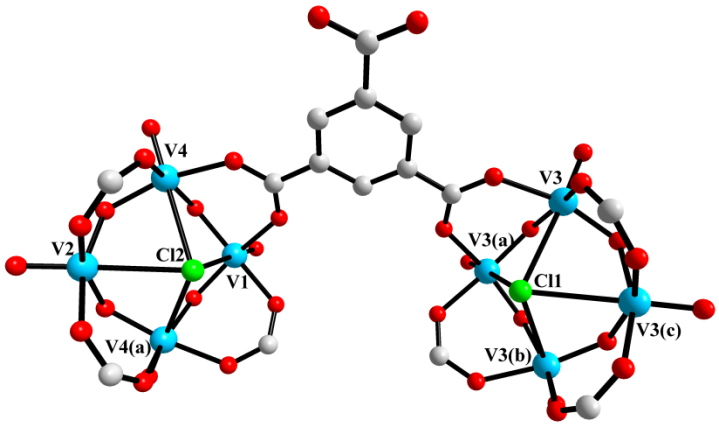

Fig. S1. Coordination environment of vanadium atoms in **Hyball-3**.

Table S1. Bond valence sum (BVS) calculation for **Hyball-3**. Calculation was performed for different oxidation state (III, IV and V). The calculated values are highlighted in yellow.

		Bond distance(Å)	V(III)	V(IV)	V(V)
V1	O11	1.591	1.508	1.6848	1.7735
	O17	1.794	0.8712	0.9733	1.0246
	O17′	1.794	0.8712	0.9733	1.0246
	O1	2.042	0.4457	0.4979	0.5242
	O1′	2.042	0.4457	0.4979	0.5242
	Cl	2.795	0.1949	0.1797	0.1797
Charge			4.3368	4.807	5.051
V2	O16	1.602	1.4639	1.6354	1.7216
	O6	1.8429	0.7634	0.8528	0.8978
	O6′	1.8429	0.7634	0.8528	0.8978
	O8	2.037	0.4518	0.5047	0.5313
	O8′	2.037	0.4518	0.5047	0.5313
	Cl	2.82	0.1822	0.168	0.168
Charge			4.0763	4.5185	4.748
V3	O12	1.601	1.4678	1.6398	1.7262
	O13	1.8163	0.8203	0.9164	0.9647
	O13′	1.8188	0.8148	0.9102	0.9582
	O10	2.0321	0.4578	0.5114	0.5384
	O11	2.0336	0.4559	0.5094	0.5362
	Cl	2.836	0.1745	0.1609	0.1609
Charge			4.1911	4.6482	4.885
V4	O4	1.6004	1.4702	1.6425	1.729
	O6	1.7873	0.8872	0.9911	1.0433
	O3	1.8442	0.7607	0.8498	0.8946
	O9	2.0276	0.4634	0.5177	0.545
	O5	2.0454	0.4416	0.4934	0.5194
	Cl	2.852	0.1541	0.1541	0.1541
Charge			4.1772	4.6486	4.885

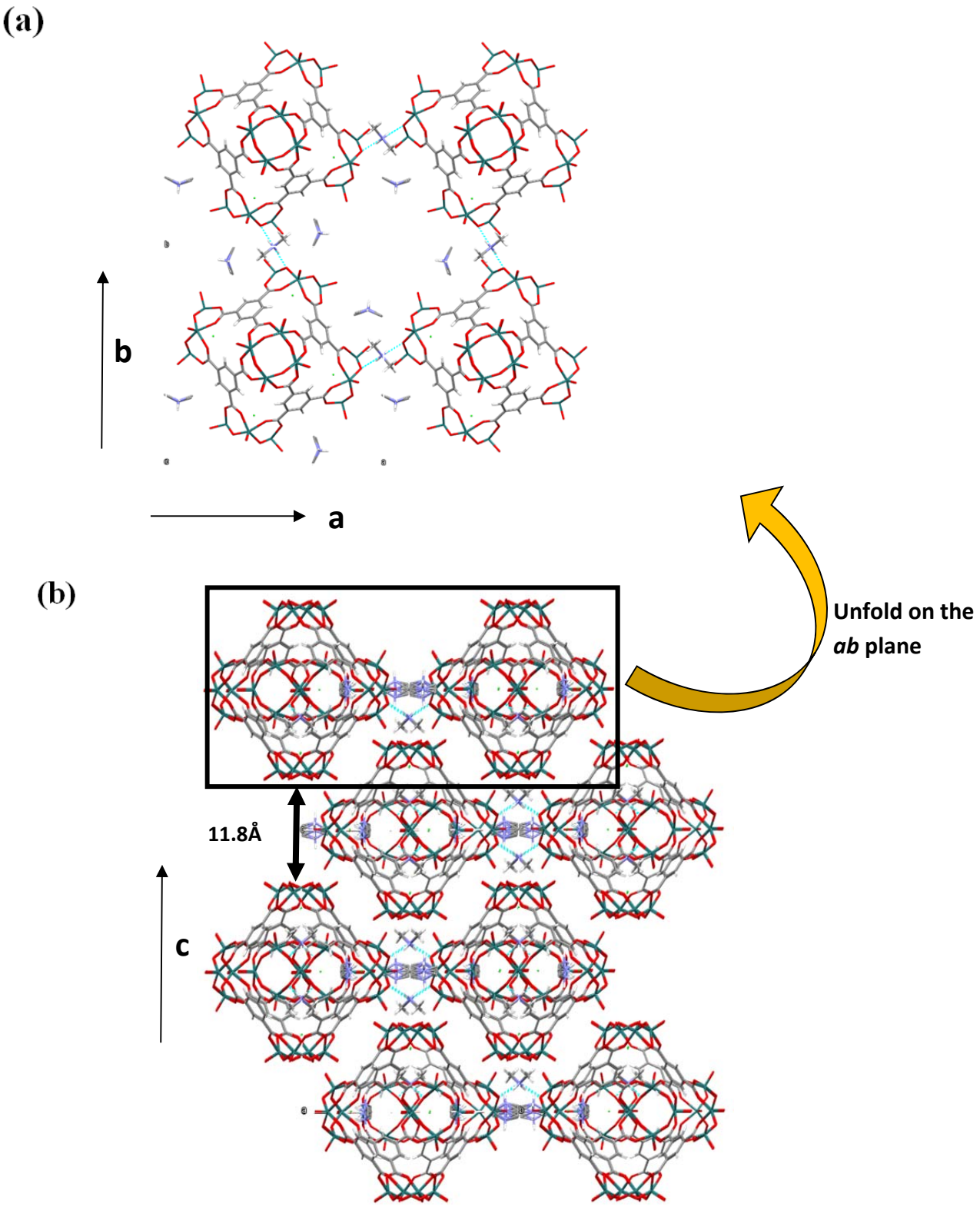

Fig. S2. (a) Hyballs are linked by dimethylammonium cations to form 2D H-bonded layers on the *ab* plane in **Hyball-3**; (c) the 2D H-bonded layers stacking with an ABA mode along the *c* direction. Hydrogen bonds are highlighted in blue dash. Solvents are deleted for clarity.

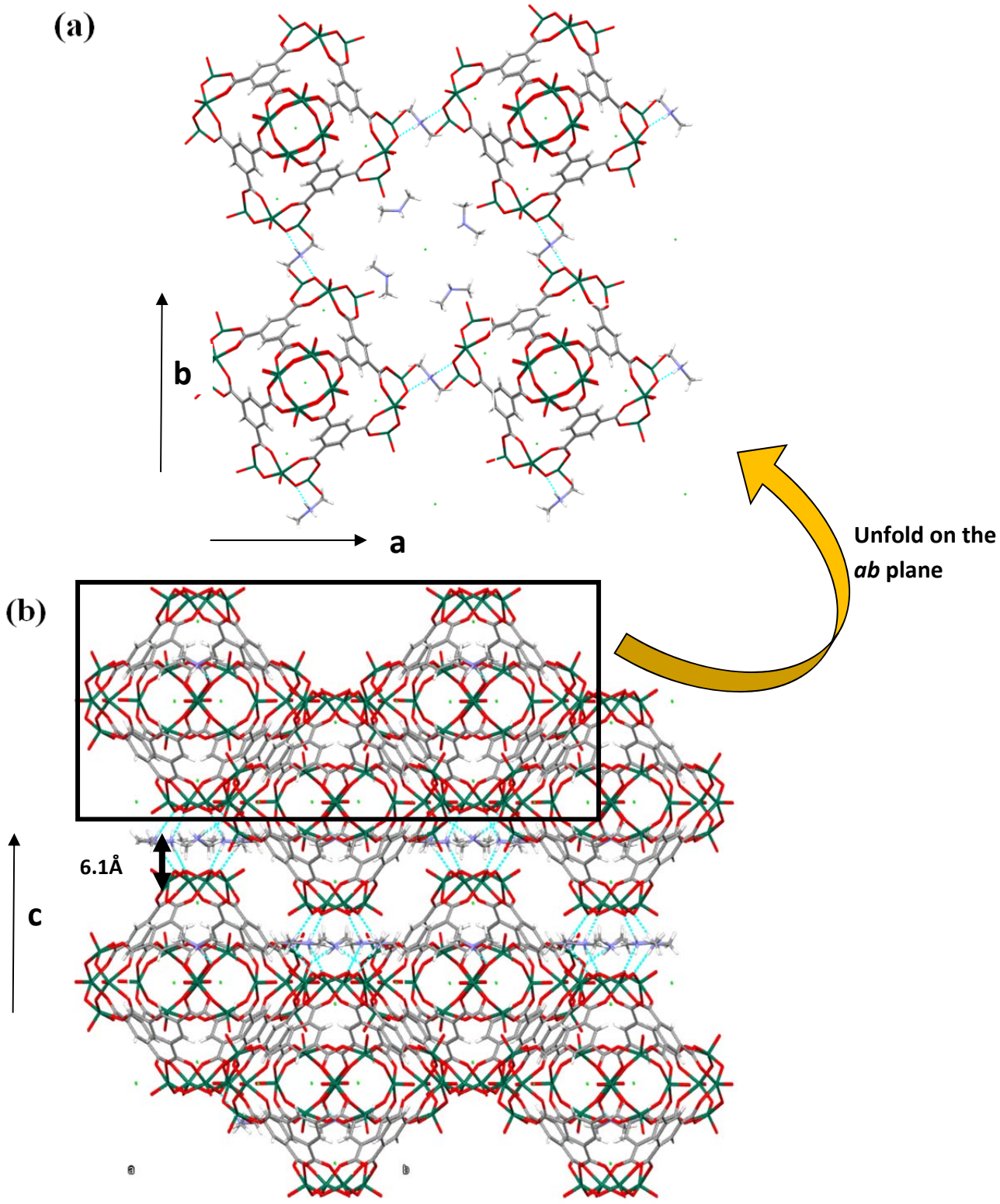

Fig. S3. (a) Hyballs are linked by dimethylammonium cations to form 2D H-bonded layers on the *ab* plane in **Hyball-3′**; (c) the 2D H-bonded layers are cross-linked by hydrogen bonds to form a 2-fold interpenetrated **pcu** net. Hydrogen bonds are highlighted in blue dash. Solvent molecules are deleted for clarity.

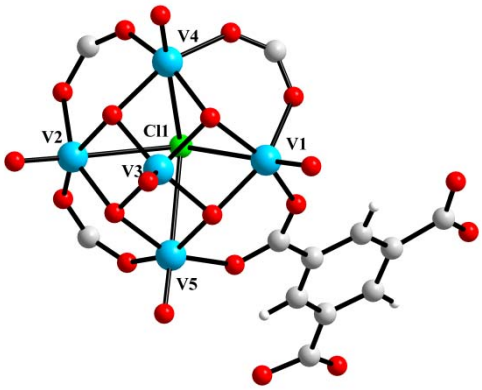

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Fig. S4. Coordination environment of vanadium atoms in **Hyball-4**.

Table S2. Bond valence sum (BVS) calculation for **Hyball-4**.

		Bond distance (Å)	V(III)	V(IV)	V(V)
V1	O16	1.6171	1.4053	1.57	1.6527
	O6	1.9051	0.6453	0.7209	0.7589
	O15	1.9468	0.5765	0.644	0.678
	O10	2.01	0.486	0.5429	0.5715
	O11	2.0836	0.3983	0.445	0.4684
	Cl	2.95	0.1282	0.1182	0.1182
Charge			3.6395	4.041	4.248
V2	O7	1.5657	1.6148	1.804	1.899
	O22	1.8285	0.7937	0.8867	0.9334
	O15	1.8396	0.7702	0.8605	0.9058
	O6	1.8694	0.7106	0.7939	0.8357
	O5	1.8732	0.7034	0.7858	0.8272
	Cl	2.975	0.0358	0.04	0.0421
Charge			4.6284	5.1708	5.443
V3	O17	1.5591	1.6438	1.8365	1.9332
	O15	1.9439	0.581	0.6491	0.6833
	O22	1.9578	0.5596	0.6252	0.6581
	O2	1.9751	0.534	0.5966	0.6281
	O9	1.9888	0.5146	0.5749	0.6052
	Cl	2.949	0.1286	0.1185	0.1185
Charge			3.9617	4.4008	4.626
V4	O4	1.6378	1.3289	1.4846	1.5628
	O6	1.9577	0.5597	0.6253	0.6583
	O3	1.9838	0.5216	0.5827	0.6135

	O9	2.0427	0.4449	0.497	0.5232
	O5	2.0739	0.4089	0.4568	0.4809
	Cl	2.977	0.1192	0.1099	0.1099
Charge			3.3832	3.7564	3.949
V5	O26	1.6198	1.3951	1.5586	1.6407
	O5	1.9481	0.5745	0.6418	0.6756
	O1	1.9529	0.5671	0.6335	0.6669
	O6	2.0096	0.4865	0.5435	0.5721
	O8	2.0537	0.4318	0.4824	0.5079
	Cl	2.943	0.1307	0.1205	0.1205
Charge			3.5856	3.9803	4.184

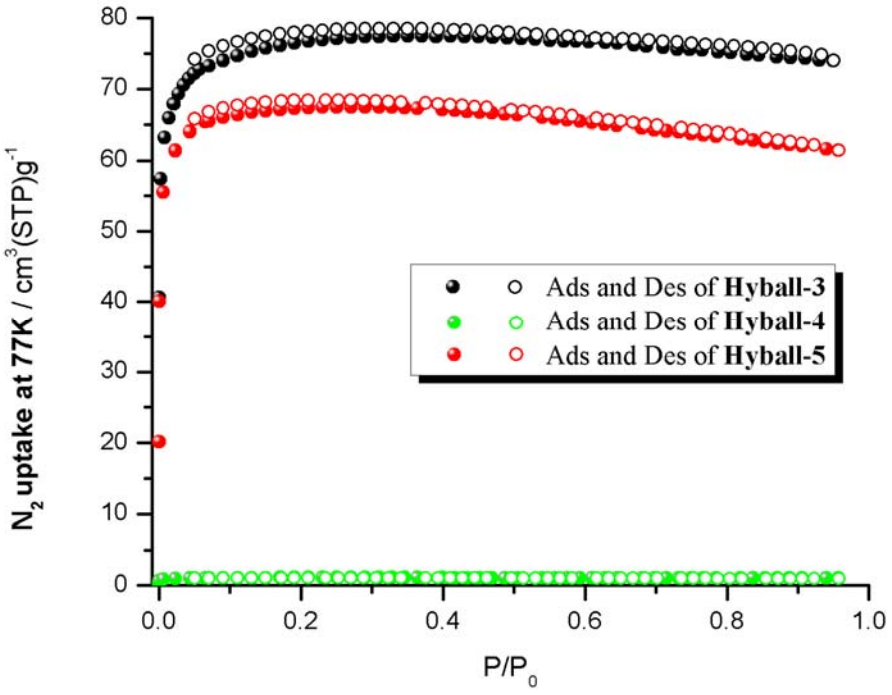

Figure S5. N_2 sorption isotherms at 77K.

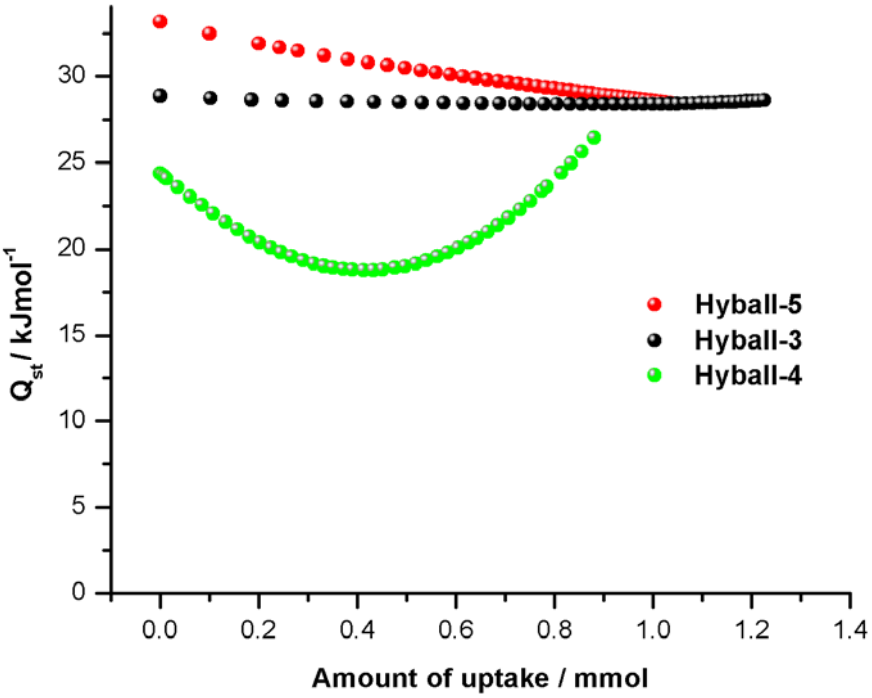

Fig. S6. Q_{st} of CO_2 for **Hyball-3**, **-4** and **-5**.

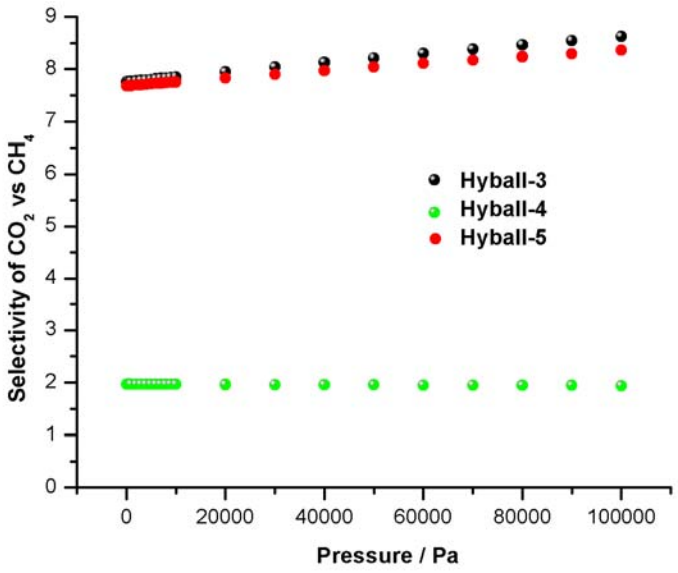

Fig. S7. IAST calculated selectivities for adsorption from equimolar gas-phase mixtures based upon the experimentally observed adsorption isotherms of the pure gases.

Ideal Adsorbed Solution Theory

Ideal adsorbed solution theory (IAST)[1] was used to predict the equimolar binary mixture adsorption of CO_2 and CH_4 from the experimental pure-gas isotherms. The single-component isotherms were fitted to a Langmuir-Freundlich equation:

$$q = q_m \cdot \frac{b \cdot P}{1 + b \cdot P} \qquad \text{(S1)}$$

Here, P is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mol/kg), q_m is the saturation capacity of adsorption (mol/kg), b is the affinity coefficient (1/kPa).

[1] Myers, A. L.; Prausnitz, J. M. *AIChE J.* **1965**, *11*, 121.

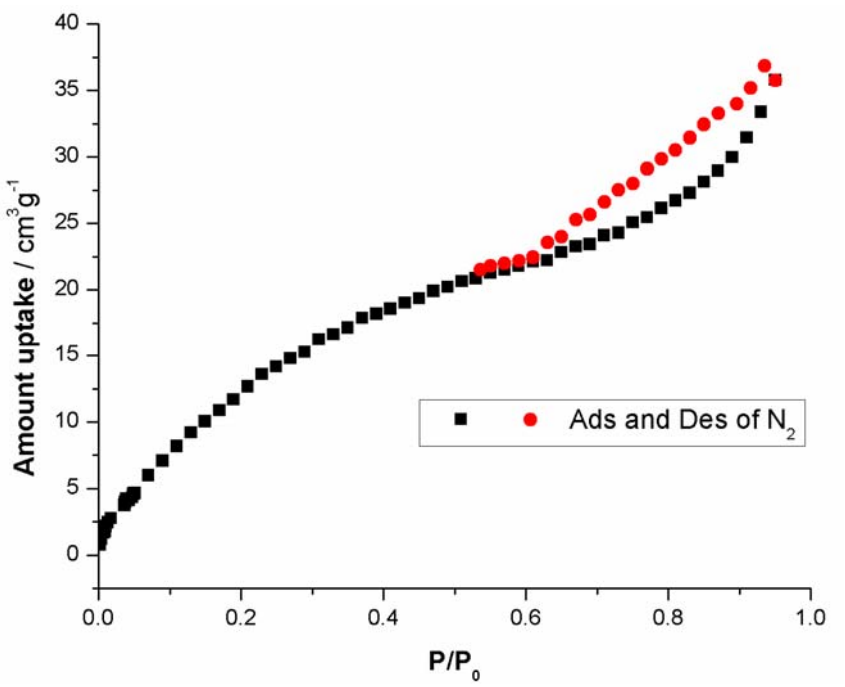

Fig. S8. N_2 sorption isotherm for **Hyball-3-Ba**.

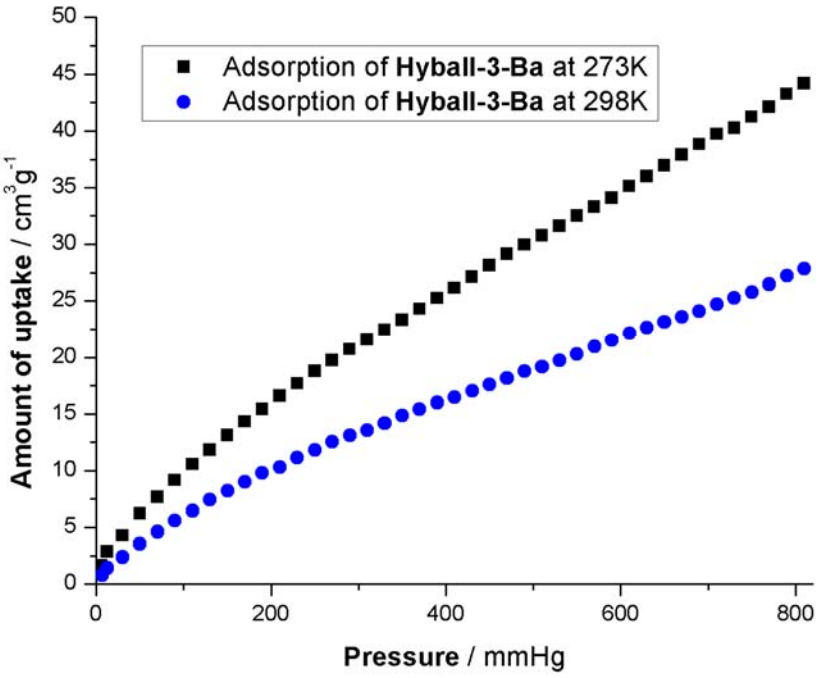

Fig. S9. CO_2 adsorption isotherm at 298K and 273K for **Hyball-3-Ba**.

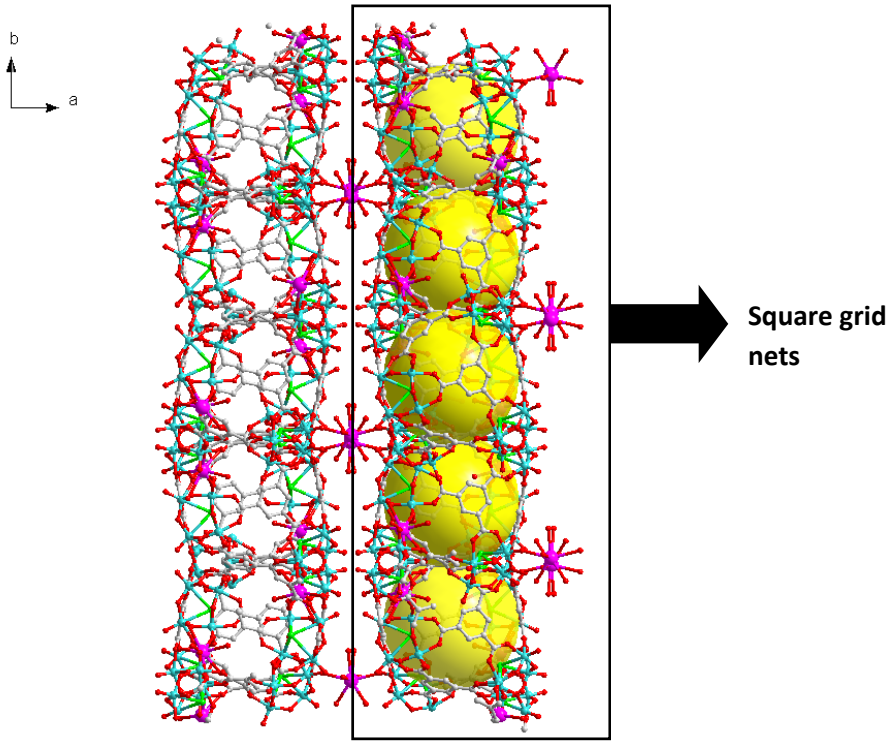

Fig. S10. The square grid nets are further linked by Ba^{2+} ions along the *a* direction to form **pcu** net in **Hyball-3-Ba**.

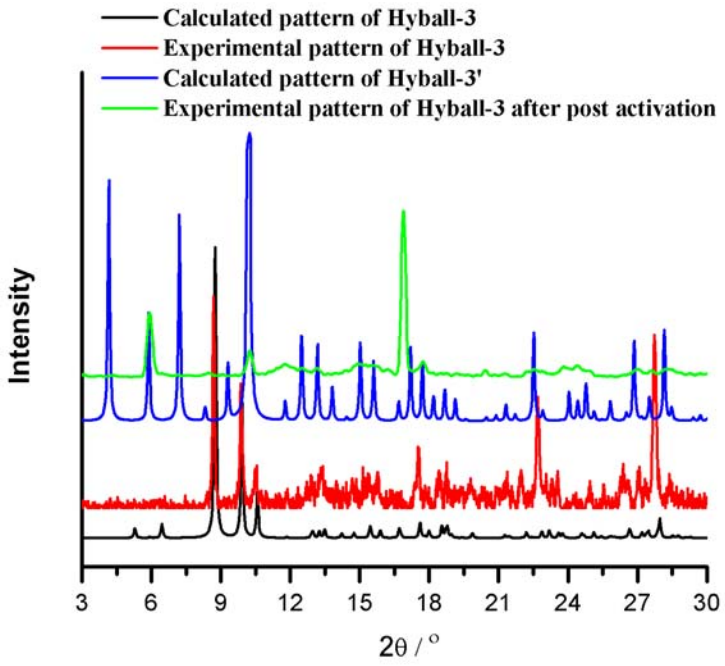

Fig. S11. PXRD patterns for **Hyball-3**.

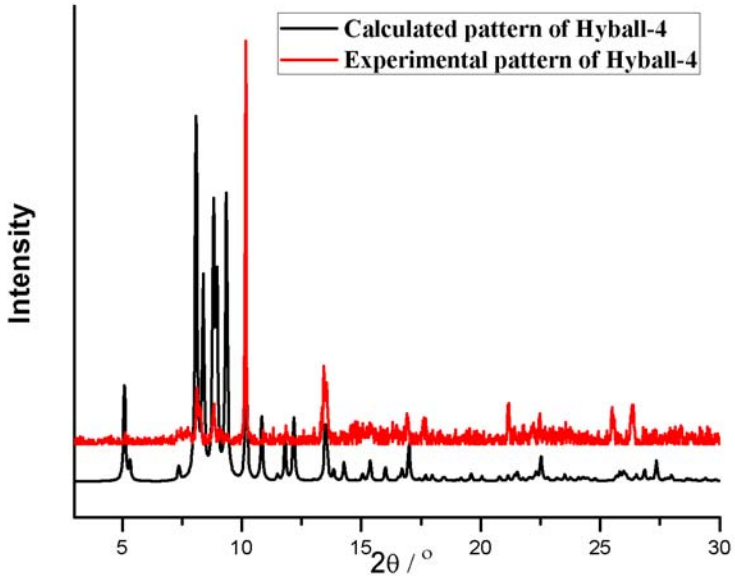

Fig. S12. PXRD patterns for **Hyball-4**.

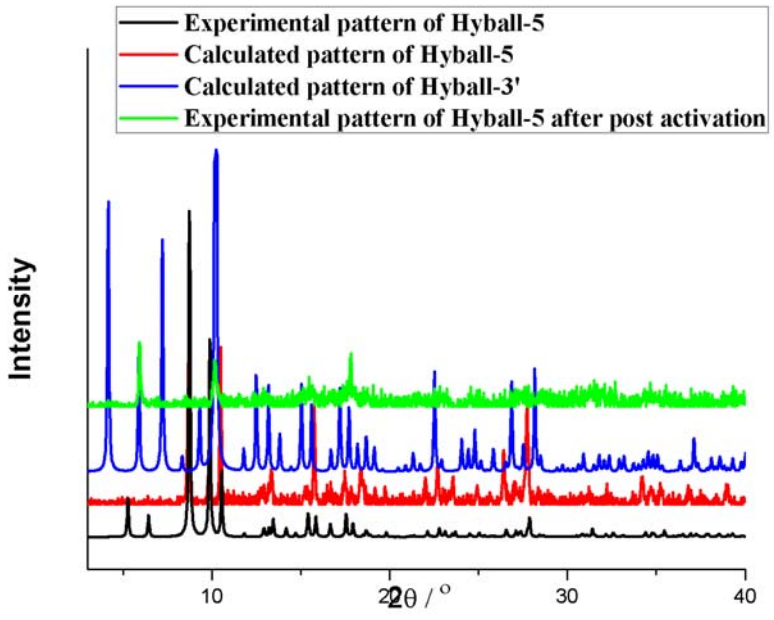

Fig. S13. PXRD patterns for **Hyball-5**.

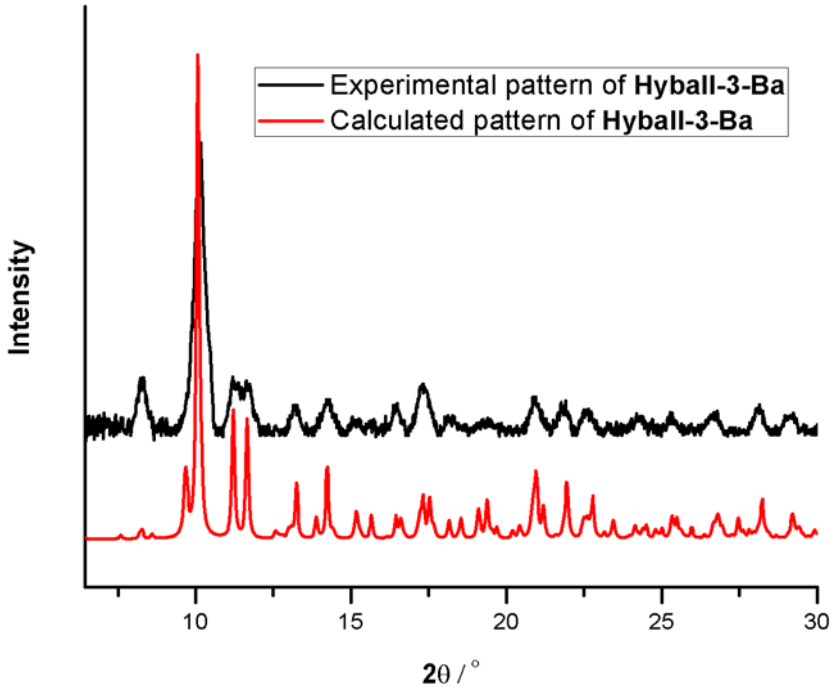

Fig. S14. PXRD patterns for **Hyball-3-Ba**.

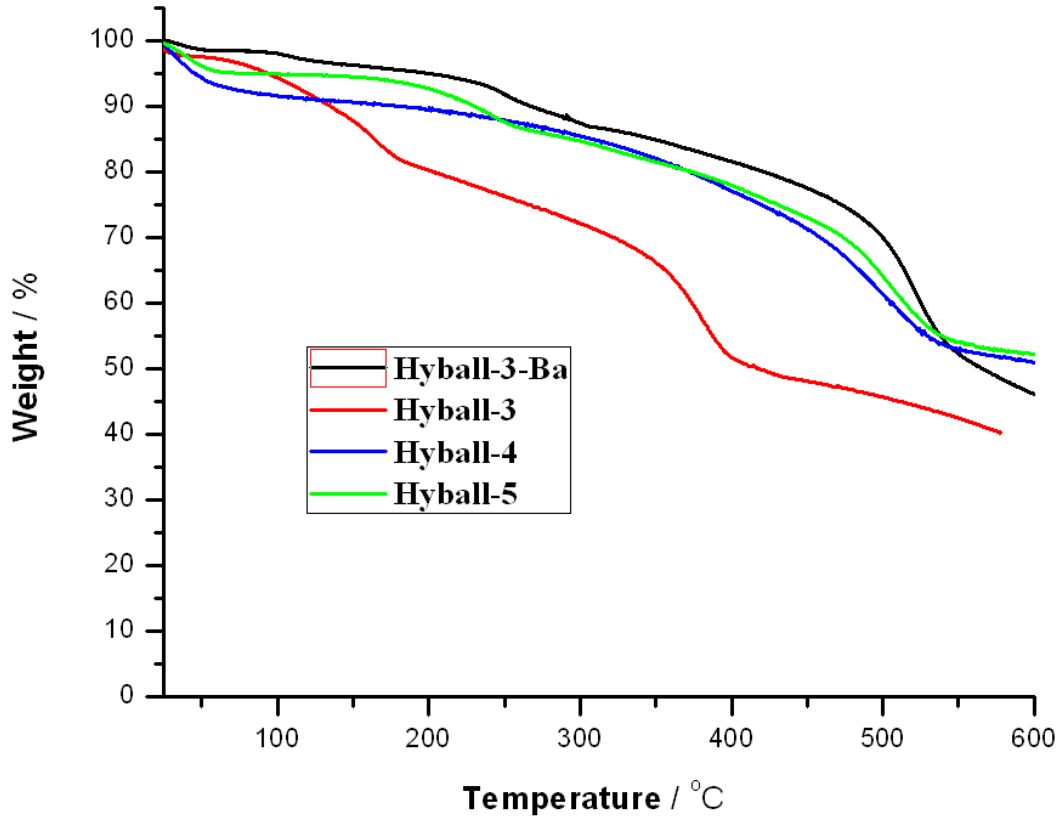

Fig. S15. TGA data for **Hyballs**.

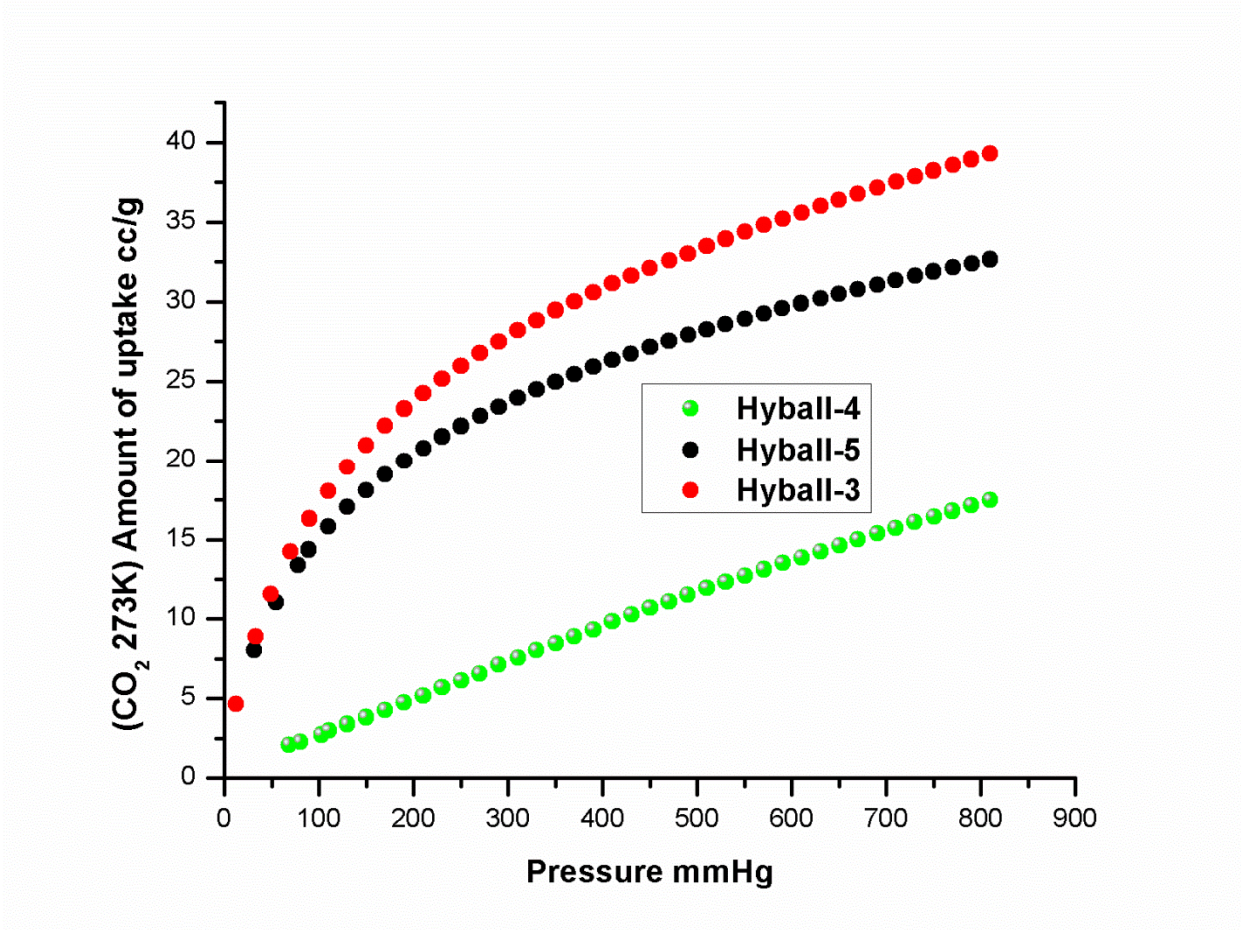

Fig. S16. CO_2 sorption isotherms at 273K.

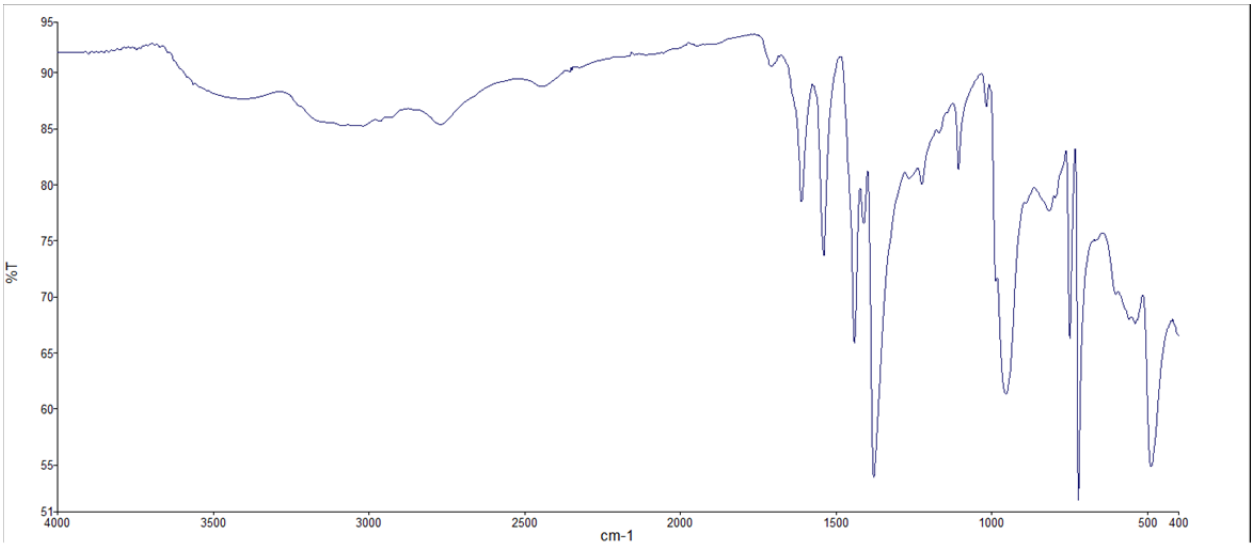

Fig. S17. IR spectra of Hyball-3.

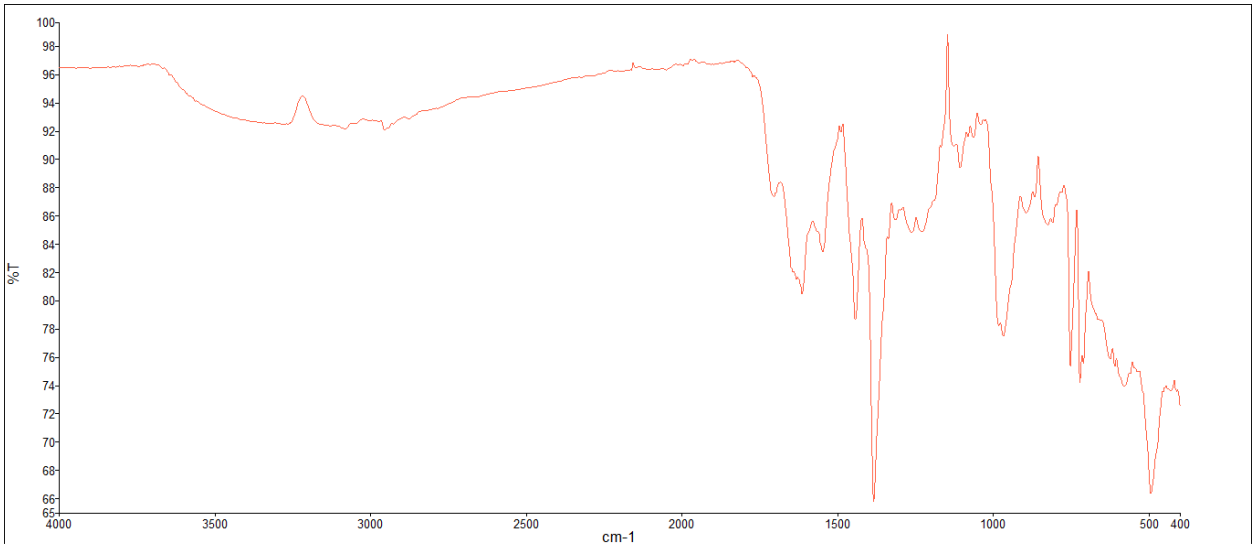

Fig. S18. IR spectra of Hyball-4.

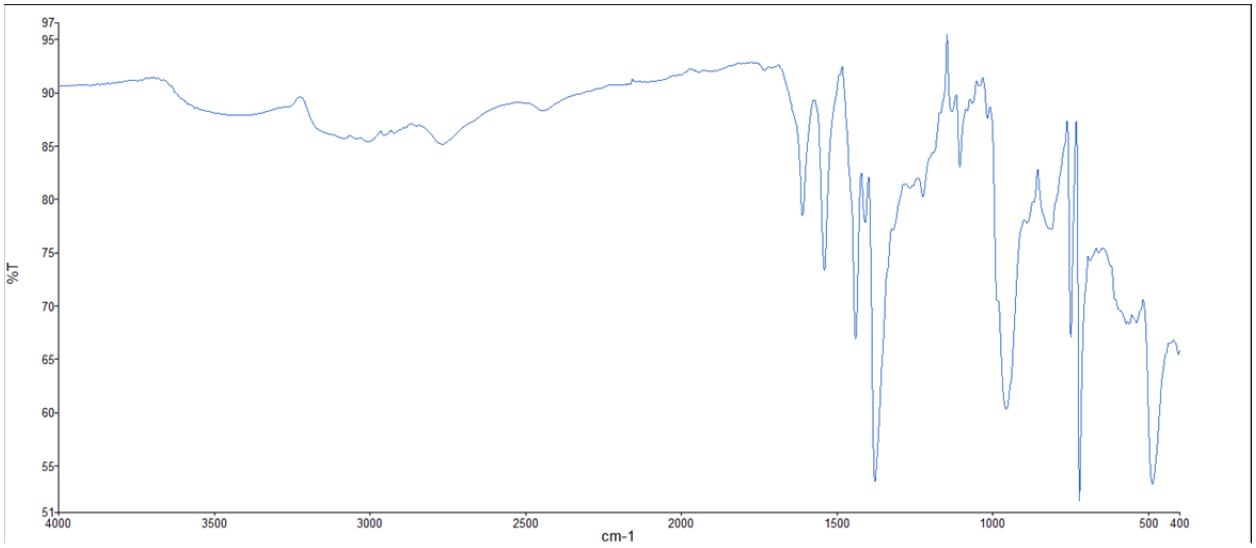

Fig. S19. IR spectra of Hyball-5.

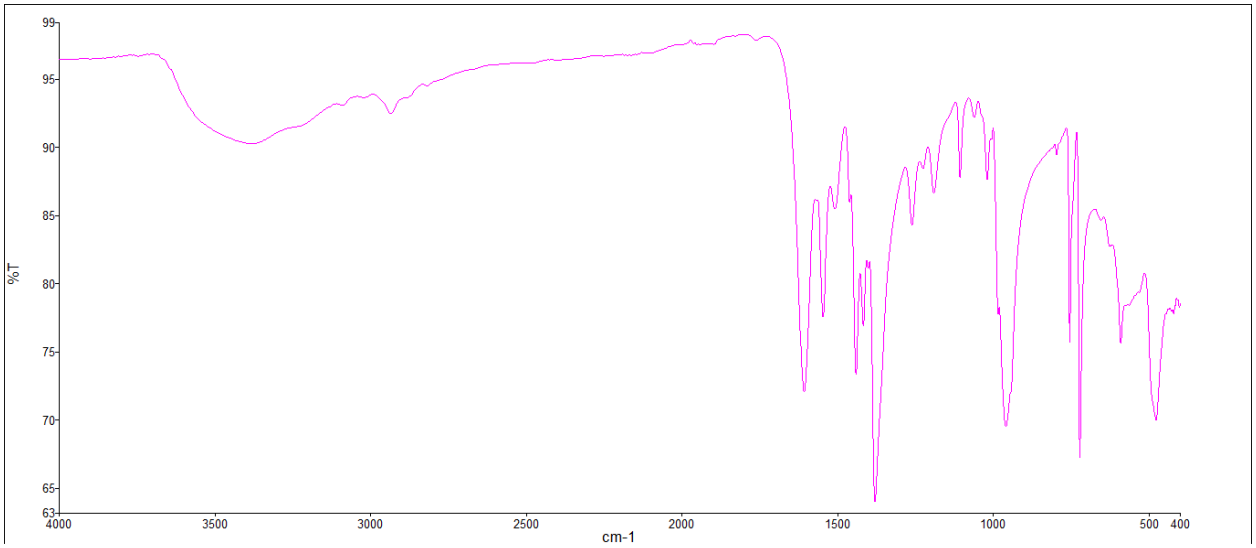

Fig. S20. IR spectrum of Hyball-3-Ba.

Table S3. Crystal data and structure refinement for Hyball-3.

Identification code	Hyball-3
Empirical formula	C10.50 H7.50 Cl0.75 N0.75 O17.88 V3
Formula weight	609.58
Temperature	100(2) K
Wavelength	0.41328 A
Crystal system, space group	Tetragonal, I4/m
Unit cell dimensions	a = 21.1256(6) A alpha = 90 deg.
	b = 21.1256(6) A beta = 90 deg.
	c = 27.4118(14) A gamma = 90 deg.
Volume	12233.6(8) A^3
Z, Calculated density	16, 1.324 Mg/m^3
Absorption coefficient	0.230 mm^-1
F(000)	4808
Crystal size	0.03 x 0.03 x 0.01 mm
Theta range for data collection	0.71 to 15.99 deg.
Limiting indices	-27<=h<=27, -14<=k<=27, -34<=l<=36
Reflections collected / unique	44178 / 7577 [R(int) = 0.0676]
Completeness to theta = 15.99	97.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9981 and 0.9942
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7577 / 12 / 368
Goodness-of-fit on F^2	1.091
Final R indices [I>2sigma(I)]	R1 = 0.0593, wR2 = 0.1797
R indices (all data)	R1 = 0.0940, wR2 = 0.2085
Largest diff. peak and hole	0.973 and -0.472 e.A^-3

Table S4. Crystal data and structure refinement for Hyball-3'.

Identification code	Hyball-3'
Empirical formula	C21 H18 Cl1.50 N1.50 O24 V6
Formula weight	1034.18
Temperature	143(2) K
Wavelength	0.71073 A
Crystal system, space group	Tetragonal, p4/n
Unit cell dimensions	a = 21.0482(14) A alpha = 90 deg.
	b = 21.0482(14) A beta = 90 deg.
	c = 21.648(3) A gamma = 90 deg.
Volume	9590.6(17) A^3
Z, Calculated density	8, 1.432 Mg/m^3
Absorption coefficient	1.275 mm^-1
F(000)	4080
Crystal size	0.02 x 0.02 x 0.02 mm
Theta range for data collection	3.14 to 23.26 deg.
Limiting indices	-12<=h<=23, -17<=k<=20, -24<=l<=22
Reflections collected / unique	17627 / 6883 [R(int) = 0.0694]
Completeness to theta = 23.26	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9750 and 0.9750
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6883 / 26 / 469
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0842, wR2 = 0.2089
R indices (all data)	R1 = 0.1681, wR2 = 0.2371
Largest diff. peak and hole	0.924 and -0.949 e.A^-3

Table S5. Crystal data and structure refinement for Hyball-4.

Identification code	Hyball-4
Empirical formula	C72 H24 Cl6 O207.75 V30
Formula weight	5953.81
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system, space group	Hexagonal, R-3c
Unit cell dimensions	a = 34.773(3) A alpha = 90 deg.
	b = 34.773(3) A beta = 90 deg.
	c = 39.676(3) A gamma = 120 deg.
Volume	41548(5) A^3
Z, Calculated density	6, 1.428 Mg/m^3
Absorption coefficient	1.122 mm^-1
F(000)	17460
Crystal size	0.02 x 0.01 x 0.01 mm
Theta range for data collection	2.99 to 20.82 deg.
Limiting indices	-32<=h<=30, -25<=k<=34, -25<=l<=39
Reflections collected / unique	18566 / 4830 [R(int) = 0.1082]
Completeness to theta = 20.82	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9889 and 0.9779
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4830 / 12 / 568
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0877, wR2 = 0.1946
R indices (all data)	R1 = 0.1954, wR2 = 0.2524
Largest diff. peak and hole	0.390 and -0.438 e.A^-3

Table S6. Crystal data and structure refinement for Hyball-5.

Identification code	Hyball-5
Empirical formula	C88 H56 Cl6 N8 O139 V26.20
Formula weight	4996.74
Temperature	396(2) K
Wavelength	0.71073 A
Crystal system, space group	Tetragonal, I4/m
Unit cell dimensions	a = 21.1683(5) A alpha = 90 deg.
	b = 21.1683(5) A beta = 90 deg.
	c = 27.3991(15) A gamma = 90 deg.
Volume	12277.4(8) A^3
Z, Calculated density	2, 1.352 Mg/m^3
Absorption coefficient	1.098 mm^-1
F(000)	4913
Crystal size	0.02 x 0.01 x 0.01 mm
Theta range for data collection	2.43 to 25.35 deg.
Limiting indices	-11<=h<=25, -25<=k<=16, -32<=l<=18
Reflections collected / unique	12758 / 5761 [R(int) = 0.0618]
Completeness to theta = 25.35	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9891 and 0.9784
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5761 / 5 / 393
Goodness-of-fit on F^2	1.144
Final R indices [I>2sigma(I)]	R1 = 0.0791, wR2 = 0.2086
R indices (all data)	R1 = 0.1395, wR2 = 0.2440
Largest diff. peak and hole	0.683 and -0.524 e.A^-3

Table S7. Crystal data and structure refinement for Hyball-3-ba.

Identification code	Hyball-3-Ba
Empirical formula	C83.50 H114.24 Ba2.50 Cl3 N12 O68.13 V12
Formula weight	3437.09
Temperature	100(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 37.3416(11) A alpha = 90 deg.
	b = 21.5080(6) A beta = 109.7710(10) deg.
	c = 36.8796(10) A gamma = 90 deg.
Volume	27873.6(14) A^3
Z, Calculated density	8, 1.638 Mg/m^3
Absorption coefficient	13.162 mm^-1
F(000)	13690
Crystal size	0.20 x 0.20 x 0.20 mm
Theta range for data collection	3.18 to 65.08 deg.
Limiting indices	-43<=h<=40, -22<=k<=24, -42<=l<=41
Reflections collected / unique	72773 / 23832 [R(int) = 0.0641]
Completeness to theta = 65.08	97.6 %
Max. and min. transmission	0.1783 and 0.1783
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	23832 / 530 / 1923
Goodness-of-fit on F^2	0.960
Final R indices [I>2sigma(I)]	R1 = 0.0742, wR2 = 0.1827
R indices (all data)	R1 = 0.0936, wR2 = 0.2061
Largest diff. peak and hole	1.409 and -2.335 e.A^-3